# Per- and Poly-Fluorinated Alkyl Substances Chemical Action Plan (PFAS CAP) – 2019 Updates

## Updated Biosolids Chapter

(minor text correction on page 6 on 3/11/19)

In 2017, the Washington State departments of Ecology and Health shared draft PFAS CAP chapters with external parties for review and comment. Comments received are available online. This document is either an update of a 2017 draft or a new 'chapter.' Ecology and Health are sharing chapters with interested parties prior to the April 2019 PFAS CAP webinar (*previously planned for March*). Updates will be discussed during the April webinar. We expect to publish the entire Draft PFAS CAP around June 2019 followed by a 60-day comment period.

In April 2019, Ecology and Health will host a PFAS CAP webinar (*date not yet set*) to:

- Briefly review activities underway: firefighting foam, food packaging, drinking water.
- Review updated/new chapters – comments will be accepted on the updated chapters. Responses will be provided after the 2019 public comment period (summer 2019).
- Discuss preliminary recommendations – requesting comments and suggestions from interested parties – due a week after the webinar.
- Submit comments online.

**Quick summary of PFAS CAP efforts:**

- PFAS CAP Advisory Committee and interested parties met in 2016, 2017 and 2018.
- September 2017 Draft PFAS CAP chapters posted:

| | |
|---|---|
| Intro/Scope | Environment |
| Biosolids | Health |
| Chemistry | Regulations |
| Ecological Toxicology | Uses/Sources |

- March of 2018, Ecology and Health published the Interim PFAS CAP.
- The 2019 updated PFAS CAP "chapters" to be posted (in the order we expect to post on the PFAS CAP website):

| | |
|---|---|
| Biosolids | *Analytical methods (new)* |
| Ecological Toxicology | Chemistry |
| Environment | *Fate and Transport (new)* |
| Regulations | *Economic analysis (new)* |
| Uses/Sources | *Preliminary Recommendations (new)* |
| Health | |

**Questions - contact Kara Steward at kara.steward@ecy.wa.gov.**

This document is posted on the PFAS CAP Website - https://www.ezview.wa.gov/?alias=1962&pageid=37105

# Appendix #: Biosolids

## Abstract

Biosolids are nutrient and organic-rich residuals from wastewater treatment. They are land applied on agricultural fields as a soil amendment and fertilizer under a regulated program. Washington's biosolids rule incorporates federal standards, requires permitting specific sites, and approval of application rates and procedures.

An extensive risk assessment was conducted by EPA prior to the promulgation of the federal biosolids rule. Three "National Sewage Sludge Surveys" have been conducted to assess contaminants in biosolids thought to pose risk to human health and the environment. Per- and Polyfluorinated Alkyl Substances (PFAS) were not evaluated under the initial risk assessment or the sewage sludge surveys even though PFAS compounds were widely used throughout the period.

Biosolids PFAS concentrations in the scientific literature have been measured using a variety of methods although the dense organic matrix has made accurate and precise results difficult to obtain. US EPA is currently validating specific methods for PFAS analysis suitable for biosolids and soil. Completion of the validation process is expected sometime in 2019.

Scientific studies evaluating PFAS from land-applied biosolids have investigated results of extremely high application rates, biosolids contaminated by direct industrial production, or used artificial spiking of PFAS compounds. These conditions are not reflective of the rates, likely concentration, or availability of PFAS in Washington biosolids under current rules.

Worldwide, concentrations of perfluorooctane sulfonate (PFOS) and perfluoroctanoic acid (PFOA) in biosolids have trended downward significantly following reduced production of these congeners. Since there is no industrial production of PFAS in Washington, exposure pathways for Washingtonians are primarily from homes and consumer products. This suggests that concentration of PFAS in Washington biosolids is from similar sources. Reduction of PFAS in consumer products will lower direct PFAS exposure and the indirect concentrations that may occur in Washington biosolids. Currently, no data exists for PFAS in Washington biosolids.

Several states in the US are considering setting PFAS contaminant levels in soil. Some leaching models used in the calculation of these limits use unrealistic values for parameters such as the fraction of organic carbon in soil ($F_{OC}$) and degree of molecular sorption ($K_{OC}$). This can result in calculating unrealistically low soil contaminant limits.

Adoption of extremely low regulatory limits for soil PFAS could have adverse consequences for organics and residual recycling. Such limits would likely interfere with established goals and benefits of recycling programs, but may not provide demonstrated risk-reduction for human health and the environment.

Risk assessment of PFAS in land-applied biosolids requires a baseline dataset for PFAS concentrations in Washington biosolids, measuring soil concentrations directly attributable to land-applied biosolids under conditions that mimic current State rules, an evaluation of contaminant modeling that uses realistic values for input parameters, and review of exposure pathways.

# Background

Amendments to the Federal Water Pollution Control Act of 1948, now known as the Clean Water Act, set in motion the creation of wastewater treatment across the US. Large scale construction of wastewater treatment plants (WWTPs) that included secondary treatment was initiated in 1972 when these facilities were nationally funded under a grant program administered by EPA.

One of the primary functions of wastewater treatment is to remove solids from the influent. Treatment plants utilize a variety of engineering designs, but most employ some sort of biological treatment whereby aquatic bacteria consume, i.e. digest, the organic constituents in the influent. The biological/organic floc along with mineral and some chemical constituents is settled out of the wastewater prior to discharge of effluent. These solids are typically high in organic matter and mechanically dewatered. Some facilities in arid climates air-dry the solids as a primary method of dewatering or in addition to a mechanical process.

In Washington, biosolids are land applied for their nutrient and soil amending properties. Land application of biosolids is conducted primarily in conjunction with commercial farming operations across the state. Department of Ecology approves individual biosolids applications on an agronomic basis—matching nitrogen needs of the crop with that supplied by biosolids. Analysis of both soil and biosolids is required by rule to calculate site-specific rates on permitted fields in advance of application.

## Federal and State Regulation

EPA administers the federal rule (40 CFR Part 503) under which specific sampling, analysis, and management is required of WWTP residuals. Requirements under the federal rule were developed during extensive scientific review and risk analysis conducted by EPA over a multi-year period preceding the adoption of the federal rule in February 1993. Under federal rules the solids generated by wastewater treatment are called "sewage sludge".

Washington regulation, Chapter 173-308 WAC-Biosolids Management, differentiates between wastewater solids that meet the regulatory standards that allow land application, classified as "biosolids", and those solids not meeting the standards that are defined as "sewage sludge". Washington law requires that *biosolids* are land applied to the greatest extent possible, but that *sewage sludge* be disposed in a landfill. Currently, about 85-90 percent of biosolids generated in Washington are land-applied [(1)].

Washington's biosolids rule adopts all the standards in the federal rule regarding sampling and analysis of WWTP solids. It imposes additional management criteria related to land application site evaluation and permitting, development of management plans that govern the land application procedures, and ongoing oversight/approval of application rates and operations.

## Biosolids Risk Assessment: Rule Development, National Surveys, and National Research Council

EPA developed the federal rule after undertaking a substantive 9-year evaluation of sewage sludge land application. This process included an "extensive multi-pathway risk assessment for evaluating and setting limits to manage pollutants in biosolids" [(2)]. It involved making a list of pollutants, developing risk-assessment methodologies, determining pollutant limits and management practices, and issuing the rule.

In 1984, EPA identified a list of 200 potential pollutants in wastewater residuals for evaluation. Included in this list were a range of toxic organics such as dioxins, furans, polyaromatic hydrocarbons, pesticides and herbicides. A scientific panel reviewed this list and made a recommendation that approximately 50 of these pollutants be evaluated for further study [(2)]. The evaluation considered toxicity, occurrence, and fate and effects of the pollutants with a focus on pathways of exposure.

In 1988, EPA conducted the first National Sewage Sludge Survey (NSSS) [(3)] in order to develop a reliable database in support of the final Part 503 biosolids regulation. Samples were collected from 180 Publically Owned Treatment Works (POTW's). These samples were analyzed for over 400 pollutants according to analytical protocols adapted specifically for the matrix of biosolids. EPA also reviewed the operational practices of 462 POTW's that utilized secondary treatment.

Following the initial survey, two subsequent National Sewage Sludge Surveys have been conducted. In 2001 the survey prioritized an evaluation of dioxins [(4)] and a *Targeted* National Sewage Sludge Survey published in 2009 [(5)] focused on pharmaceuticals and personal care products. Although in wide use at the time, neither per- and polyfluorinated alkyl substances (PFAS) as a chemical group, nor the specific congeners *Perfluorooctane Sulfonate* (PFOS) and *Perfluoroctanoic Acid* (PFOA) were evaluated.

The National Research Council (NRC) has twice reviewed the federal rule, 40 CFR Part 503. In 1996 the NRC released "Use of Reclaimed Water and Sludge in Food Crop Production" and in 2002 reviewed the science and methodology underlying the health and environmental standards entitled "Biosolids Applied to Land: Advancing Standards and Practices". Both studies concluded that the federal rule was protective of human Health and the environment, but *Per- and Polyfluorinated Alkyl Substances* (PFAS) were not specifically part of these evaluations. The 2002 NRC review stated that "there is no documented scientific evidence that the Part 503 rule has failed to protect public health".

Pursuant to the Clean Water Act Section 405(d), EPA must review the biosolids regulations every two years. They are directed to identify additional toxic pollutants that show sufficient evidence of harm and establish management practices protective of human health and the environment. An international study in 2011 stated that research on organic contaminants in biosolids has been undertaken for over 30 years and the increasing body of evidence demonstrates that the majority of compounds studied do not place human health at risk when biosolids are land applied on farmland [(6)]. The study cautions that "continued vigilance in assessing…'emerging' organic contaminants in sludge is necessary to support and ensure the long-term sustainability and security of the beneficial agricultural route for biosolids management."

## WWTP Residuals: PFAS Analysis Methods, Concentration, and Trends

The required analytical methods and analytes for WWTP residuals in the US are specified by EPA in the federal rule (40 CFR Part 503) and incorporated into the Washington State rule (Chapter 173-308 WAC). Municipalities are required to test their biosolids for a range of chemical parameters including nutrients and regulated metals. The frequency of testing is determined by the quantity of biosolids the facility generates with larger facilities required to conduct more frequent testing.

Regulatory analysis of biosolids in Washington State is required to be conducted by laboratories accredited by the Department of Ecology. WWTP residuals in Washington state are considered sewage sludge until they are analyzed by accredited labs using specified methods with the results meeting minimum standards. Residuals meeting the standards in the Washington rule are deemed biosolids and required to be beneficially used.

Wastewater residuals are a dense organic matrix and have proved difficult to accurately analyze. EPA spent considerable time developing the appropriate methodologies required in the federal rule in order to achieve accurate and consistent results. Laboratories often commit the analytical error of conducting biosolids analyses using methods developed for water and wastewater [(7)].

EPA has developed Method 537 for analyzing PFOS, PFOA, and 12 other PFAS in drinking water [(8)]. Some US labs are analyzing biosolids using modified procedures based on EPA Method 537, but guidelines are inconsistent and results have not been validated [(9, 12)]. Department of Ecology's lab accreditation unit at Manchester Environmental Laboratory has performed a technical review of one laboratory in Washington for analysis of a limited number of PFAS compounds in Solids and Chemical Materials using a modified 537 method. Manchester has also recognized the accreditation of the National Environmental Laboratory Accreditation Program (NELAP) for a few other Washington laboratories for PFAS analysis in the solids and chemical materials matrix using modified 537 methods [(10)]. Such accreditation assures that the procedures are being appropriately followed, not that the method provides the most accurate and consistent results when analyzing biosolids.

EPA is in the process of validating a different procedure for analyzing biosolids and soil for PFAS, SW-846. Phase I was carried out in the winter of 2017 for 24 PFAS in various media. Phase II of this process is currently underway in the fall of 2018 and several external labs are in the process of validating these procedures for public review [(9)]. It is unlikely that EPA will have finalized its approval of method(s) for PFAS analysis in biosolids before 2019 [(11)(12)].

Separate from the SW-846 analysis procedures being reviewed by EPA, is another analysis method for PFAS, Total Oxidizable Precursor (TOP) assay. This method uses a chemical oxidation pretreatment. While a number of commercial labs offer the TOP assay, the oxidation can be more or less "aggressive" depending on the details of the procedure [(13)], but there is no currently settled methodology or agreed "best" approach.

The concentration of PFOS/PFOA in biosolids has been reported from a variety of sources outside of Washington State [(14, 15, 16, 17, 18, & 19)] with PFOS often being the most abundant [(15, 19)]. Four WWTPs in Washington had effluent analysis for PFOS/PFOA, but this review did not include an analysis of biosolids for these compounds [(20)]. In general, the chemistry of biosolids is reflective of the chemistry of our daily lives as is the dust in our homes [21][22]. Washington residents are exposed to PFAS from carpets, food packaging, personal care products and cosmetics, surface coatings on textiles, paints, lubricants, waterproof fabric, ski wax, and wide variety of other sources so it would not be surprising if there were trace amounts in Washington biosolids.

Industrial sources of perfluoroalkylates can influence concentrations of these compounds in biosolids when a wastewater treatment plant receives influent directly from industries that work with fluorotelomer compounds. A WWTP in Decatur, Alabama received effluent from industries that conducted electrochemical fluorination and worked with a variety of fluorotelomer compounds and perfluoroalkylates [23]. The data for PFOA concentrations from Decatur sewage sludge are fragmentary, but show high levels in years 2005 and 2006: 528 ng/g & 683 ng/g in 2005, and 1,875 ng/g in 2006. Subsequent to significant reduction from industrial discharges the concentration of PFOA in the Decatur biosolids decreased markedly. Data available from Decatur sewage sludge produced in 2008 indicate PFOA concentrations in biosolids of 27 and 32 ng/g [24].

Washington State does not have commercial production of perfluorochemicals. Additionally, industrial discharges receive pretreatment prior to discharge to domestic wastewater treated at the 300 + wastewater treatment plants in the state that produce biosolids for land application. This suggests that the vast majority of perfluorinated compounds in Washington municipal wastewater would originate from domestic sources—our homes and consumer products. Contamination such as that identified in Alabama biosolids is highly unlikely to occur in Washington.

A trend of decreasing concentrations of PFOA/PFOS is observed across a broad spectrum of data characterizing biosolids using a variety of analytical methods. A review of sewage sludge analysis in Germany evaluated perfluoroalkyl acids (PFAAs) concentration from 4981 samples from 1165 WWTPs collected between 2008 and 2013 [18]. Seventy-one WWTPs had samples exceeding an EU precautionary level of 125 ug/kg, but this occurred with decreasing frequency over time. The exceedances decreased from 6 percent in 2008 to 0.8 percent in 2013 and WWTPs uncontaminated with PFOS/PFOA increased by 32 percent. In the samples evaluated, PFOS was found in 41 percent and PFOA in 7 percent. 47 percent of WWTPs showed clear decreases over time and 16 percent showed an increasing trend. The total load of PFAAs in sewage sludge was reduced by over 90 percent during this time period. These reductions are likely the result of the production decrease regarding PFOS and PFOA.

In 2013 archived samples of biosolids from the EPA National Sewage Sludge Survey in 2001 were combined into 5 composite samples and analysis showed concentrations of PFOS at 403 +/- 127 ng/g, and PFOA at 34 +/- 22 ng/g, [16]. These archived NSSS samples represented 94 WWTPs in 32 states, but did not include Washington State. A summary of perfluorinated compounds (PFCs) in sewage sludge from 2005 to 2015 monitoring data worldwide was compiled by carbon chain length at concentrations of ng/g [19]. With few exceptions, these more recent samples are lower for PFOS and PFOA than the composite results from samples in the EPA National Sewage Sludge Survey of 2001. A reduction in PFOS and PFOA levels in human blood [25] was also observed in data compiled from the National Health and Nutrition Examination Surveys (NHANES). They conclude this is “most likely related to discontinuation in 2002 of industrial production…of PFOS and related perfluorooctanesulfonyl fluoride compounds".

## Literature Review of Biosolids Land Application Effects

In the well-known case from Decatur, Georgia (referenced above), biosolids were land applied to about 2000 ha of agricultural fields for over a decade [23]. The elevated levels of perfluoroalkylates (PFAs) in the biosolids generated concern that land application may constitute a pathway to contaminate surface and ground water. In order to evaluate this risk, EPA collected some initial soil samples in 2007 from Decatur land application sites and from nearby "background" fields that did not receive biosolids. Results indicated the presence of high concentrations of several fluorotelomer alcohols (FTOHs) and PFAS in soil. After collection of these initial soil samples and public drinking water samples, EPA collected an expanded set of soil samples in 2009 to more accurately characterize the extent of contamination in and around the land application sites. These land application activities and the EPA review has received widespread coverage in news reports and has been noted in a variety of websites [26, 27, & 28].

The soil from sludge-applied fields in Alabama had PFAS concentrations that were higher than the background field samples. The highest PFOA concentrations from sludge-applied fields were ≤320 ng/g and PFOS ≤410 ng/g. Annual biosolids application rates of Decatur biosolids for a 5-year period between 2002 and 2006 ranged from 14.9 to 43.9 megagrams per hectare (Mg/ha). These amounts are well above Washington's mean application rate of 6.95 Mg/ha calculated from 809 regulatory approvals for land application of biosolids for Alfalfa/grass hay, barley, canola, corn, hops, sunflowers, triticale, and wheat over the years 2010 to 2017 for which data are available [29]. The minimum Decatur rate exceeds all but 6 of the 809 Washington approvals. The six higher land application rates approved in Washington were for lagoon biosolids that contained significant amount of mineral material (sand) and low nitrogen content. From the perspective of an agronomic evaluation, rates used for the Decatur biosolids would have likely resulted in excessive N accumulations and leaching of nitrate. Such rates would be unlikely to receive regulatory approval in Washington.

Sepulvado et al land applied municipal biosolids from Chicago to investigate questions about the fate of perfluorochemicals [15]. This investigation indicated four significant results: Concentrations of PFC's in soil increased linearly with increasing biosolids loading rate (PFOS 2-483 ng/g), desorption experiments indicated that the leaching potential of perfluorochemicals decreased with increasing carbon chain length, previously derived organic carbon partition coefficients may not be accurate predictors of the desorption of long-chain PFCs, and trace levels of short-chain PFCs were detected in soil cores below the level of incorporation.

The Chicago biosolids in the Sepulvado study were land applied at very high cumulative loading rates. Their long-term plots had applications over 32 years amounting to 553 Mg/ha (low rate), 1,109 Mg/ha (medium rate) and 2,218 Mg/ha (high rate) [15]. Although the PFAS soil concentrations were linearly correlated with application rates, the loading rates in the Sepulvado study were significantly higher than the mean Washington agronomic rate of 6.95 Mg/ha. It would require 79, 159, and 319 years of annual applications respectively at Washington's average application rate to achieve similar cumulative loading. However, most fields in Washington do not have biosolids applied annually. On a wheat-fallow rotation applications are made every other year at most, and commonly every 4th year. Applications on alternate years would require a minimum of 158 years to achieve the lowest cumulative biosolids loading in the Sepulvado study. These were biosolids likely to have far higher levels of PFOS/PFOA than in Washington biosolids due to the dates when they were produced and potential industrial contamination.

In a spiked soil study, Stahl, et al [(30)] reported bioaccumulation and that PFOA and PFOS at very high concentrations can result in diminished growth of spring wheat. However, spiked-soil studies are known to create results not seen in field investigations with typical agronomic application rates. Higgins notes that spiked-soil studies are known to be problematic regarding contaminant transfer [(31)]. Similarly, regarding metal uptake, Brown et al [(32)] demonstrated that "significantly less cadmium was taken up by lettuce grown on biosolids amended soil than lettuce grown on soil amended with equivalent rates of a Cd salt."

Negative impacts on crop growth are not representative of yield data from biosolids applications in Washington State. Results from a long-term Washington State University study site evaluating biosolids applications to winter wheat and canola have shown significant long-term yield *increases* from biosolids applications compared with the control or mineral fertilizer additions [(33)]. This is despite the fact that there are likely to be trace amounts of PFAS in the biosolids. However, there are no PFAS soil concentration data from this site nor has EPA addressed agricultural soil concentration limits to date.

In a widely distributed greenhouse and field study of plant uptake of perfluoroalkyl acids (PFAAs) from biosolids, Higgins et al [(31)], looked at PFAA concentrations in lettuce *(Lactuca sativa)* and tomato *(Lycopersicon lycopersicum)* grown in biosolids amended soils. The greenhouse portion of the study used industrially impacted biosolids, biosolids from a long-term application site, as well as 'clean' soil. They calculated bioaccumulation factors (BAFs) looking at concentrations in soil relative to plant concentrations primarily from the greenhouse portion of the trial. They conclude that "This study confirms that the bioaccumulation of PFAAs from biosolids-amended soils depends strongly on PFAA concentrations, soil properties, the type of crop, and analyte".

In Higgins "field scale trial" using lettuce and tomato, and a "full-scale field study" with corn, the plant concentrations were below the level of quantification (LOQ) for all treatments except the 4x agronomic rate (100 Mg/ha), which is 14x the average application rate in Washington. Given the results of the Higgins study, it is highly unlikely that grain would exhibit concentrations above the LOQ as a result of agronomic applications in Washington where PFOS/PFOA concentrations are likely to be very low due to pretreatment and no industrial manufacturing.

The Higgin's greenhouse study shows how small-scale investigations into bioaccumulation can differ significantly from regulated, field-scale applications in Washington. Higgins used 3 types of soil: control, "Industrially impacted", and "municipal". The industrial soil was created by adding a 10% (dry weight) biosolids compost and the municipal soil originated from cumulative applications of municipal biosolids that totaled 1654 Mg/ha. The industrially impacted soil had concentrations of PFOA 78.5 ug/kg and PFOS of 49.7 ug/kg and the municipal soil had concentrations of PFOA 14.9 ug/kg and PFOS 319.5 ug/kg. In both cases soil concentrations are orders of magnitude higher than would realistically result in Washington state from agronomic biosolids applications. Indeed, it would be impossible to reach the PFAS soil concentrations seen in the Higgins study if initial biosolids concentrations are significantly lower than those modeled. Tables 1 and 2 show the time necessary to reach such concentrations using biosolids PFAS concentration data from the literature combined with the mean Washington biosolids application rate. *Actual* PFAS concentrations in Washington biosolids are likely to be significantly lower than these values.

TABLE 1: Estimates of the time needed to reach Higgins, et al "Municipal" soil concentrations from annual applications of biosolids using various concentration estimates and mean Washington application rate in megagrams per hectare (6.95 Mg/ha).

| Biosolids PFOS[a]/PFOA[b] Concentration | Biosolids Application Rate[(18)] | PFOS/PFOA Applied per Application-Dry Weight | Soil Depth | Soil Weight/ha | Calculated Soil Conc. | Higgins et al Municipal Soil Conc. | Years To Reach Soil Levels* |
|---|---|---|---|---|---|---|---|
| 19/10 ug/kg ***Ulrich*** *[(9)]* | 6.95 Mg/ha | [a]132,050 ug<br>[b] 69,500 ug | 15 cm | 2,000,000 kg | 0.066 ug/kg<br>0.035 ug/kg | 319.5 ug/kg<br>14.9 ug/kg | [a] **4,841**<br>[b] **426** |
| 32 ug/kg PFOA ***Wash. et al*** *[(12)]* | 6.95 Mg/ha | 220,400 ug | 15 cm | 2,000,000 kg | 0.110 ug/kg | 14.9 ug/kg | [a] **135** |
| 403/34 ug/kg ***EPA Composites 2001***[(7)] | 6.95 Mg/ha | [a]2,800,850 ug<br>[b] 236,300 ug | 15 cm | 2,000,000 kg | 1.400 ug/kg<br>0.118 ug/kg | 319.5 ug/kg<br>14.9 ug/kg | [a] **228**<br>[b] **126** |

* One application annually, summed empirical amounts only (No degradation or leaching of PFOS/PFOA). Application rates are Megagrams per hectare (Mg/ha).

TABLE 2: Estimates of the time needed to reach Higgins, et al "Industrial" soil concentrations from annual applications of biosolids using various concentration estimates and mean Washington application rate in megagrams per hectare (6.95 Mg/ha).

| Biosolids PFOS[a]/PFOA[b] Concentration | Biosolids Application Rate[(18)] | PFOS/PFOA Applied per Application-Dry Weight | Soil Depth | Soil Weight | Calculated Soil Conc. | Higgins et al "Industrial" Soil Conc. | Years To Reach Soil Levels* |
|---|---|---|---|---|---|---|---|
| 19/10 ug/kg ***Ulrich*** *[(9)]* | 6.95 Mg/ha | [a]132,050 ug<br>[b] 69,500 ug | 15 cm | 2,000,000 kg | 0.066 ug/kg<br>0.035 ug/kg | 49.7 ug/kg<br>78.5 ug/kg | [a] **753**<br>[b] **2,243** |
| 32 ug/kg PFOA ***Wash.*** *[(12)]* | 6.95 Mg/ha | 220,400 ug | 15 cm | 2,000,000 kg | 0.111 ug/kg | 78.5 ug/kg | [a] **707** |
| 403/34 ug/kg ***EPA Composites 2001***[(7)] | 6.95 Mg/ha | [a]2,800,850 ug<br>[b] 236,300 ug | 15 cm | 2,000,000 kg | 1.400 ug/kg<br>0.118 ug/kg | 49.7 ug/kg<br>78.5 ug/kg | [a] **36**<br>[b] **665** |

* One application annually, summed empirical amounts only (No degradation or leaching of PFOS/PFOA). Application rates are Megagrams per hectare (Mg/ha).

# Factors Influencing Risk Assessment of PFAS in Washington Biosolids

## PFAS Concentration Data

PFOS was voluntarily phased-out of production in the US between years 2000 and 2002 by its primary producer 3M Company [(34)]. Since 2006, eight global manufacturers have participated in a voluntary phase-out of PFOA by 2015 [(35)]. Reduced production of PFOS & PFOA is likely the reason for the lower reported concentrations of these chemicals in sewage sludge and biosolids in recent years. The biosolids PFOS/PFOA data in Germany [(18)] and locations worldwide [(19)] using a variety of analytical methods suggest that concentrations of these chemicals are trending downward.

There is currently no PFAS data from biosolids generated in Washington. In June 2018 regulators and officials from major producers of biosolids across the state discussed the issue of PFAS data. There were a number of unresolved issues regarding how samples would be collected, what analysis method(s) would be used, who would pay for any analysis, data use and evaluation, and public dissemination of proprietary analysis results.

PFAS data in the literature from biosolids outside of Washington has been obtained using a variety of analytical methods. The accuracy and precision of these data is uncertain considering that EPA has not concluded its validation of analysis methods in a biosolids or soil matrix. It is "virtually impossible" to correlate PFAS soil data gathered across different states that have used various sample collection procedures and non-validated analysis methods [(36)].

Some commercial laboratories are claiming they can measure PFAS in solid matrices (biosolids & soil) at reporting limits as low as 0.2 ug/kg (ppb). Claims of such precision in analysis results are suspect because actual lab results often show Reporting Limits in the range of 2 – 5 ppb. Different methods also show wide variation in results. For example, Vermont DEC conducted split sample tests comparing a DOD-preferred isotope dilution method (MLA 110) with a "modified Method 537" [(37)]. When analyzing wastewater they found differences in results ranging from 10% - 200%. When analyzing wastewater solids the range of difference between the methods exceeded 300%.

## Modeling Data

New York and Maine have made attempts at groundwater migration models to estimate leaching of PFAS in soil. The models used to derive soil screening values have not been field-verified for the PFAS chemicals and there is insufficient published research on soil leaching of biosolids-sourced PFAS to allow for robust understanding of the potential leaching risks.

The sorption of perfluorinated compounds to soil influences their fate and distribution in the environment after land application. There is evidence that PFOS/PFOA persistence in soil is related to carbon-chain length with longer carbon-chains being more persistent and less mobile in soil [(15, 23)]. Laboratory determined organic-carbon partitioning coefficients ($K_{OC}$) are often used to predict potential mobility of organic contaminants in the environment [(38)]. $K_{OC}$ values can vary based on the method used for calculation [39] and derived values appear to differ from gross distribution of PFAS compounds in the environment. Lab-based Log $K_{OC}$ values may overestimate PFOS/PFOA concentrations in water and underestimate soil residence time [17].

Determining $K_{OC}$ values that are reflective of the environmental fate of biosolids-sourced PFAS compounds has proven difficult. It is likely that the database for $K_{OC}$ values for the range of perfluorinated compounds is incomplete and may not provide adequate information to accurately model movement in a soil system. Given that biosolids are settled out of an aqueous media, PFAS congeners with lower sorption are likely to leave wastewater treatment in the effluent. This may reduce overall PFAS amounts and provide an inherent bias for higher sorption congeners (higher $K_{OC}$) to remain in biosolids. This may result in reduced mobility of biosolids-sourced PFAS relative to the suite of PFAS congeners found in the WWTP influent. Thus, field-scale studies investigating the transfer or leaching of biosolids-sourced PFAS in natural soil systems are important to evaluate actual mobility and risk from biosolids land application.

Leaching models use a number of factors including the Fraction of Organic Matter ($F_{OC}$) in soil and $K_{OC}$. Small changes in these factors directly affect model outcomes. Alaska Department of Environmental Conservation (ADEC) is currently evaluating soil standards based on a leaching model where the $F_{OC}$ is assumed to be 0.1%. This is an unrealistic value associated with land applied biosolids where PFAS compounds would be, a) land applied in a dense, organic-matter matrix, and, b) likely be applied to soils with significantly higher organic matter content. The Alaska model also used EPA's lab-based log $K_{OC}$ values that are not field verified. ADEC's on-line calculator run with more realistic inputs for organic content and partitioning coefficients resulted in significantly higher calculated soil PFAS limits [40].

Data and modeling uncertainties inhibit accurate assessment of risk to human health and the environment from biosolids-sourced PFAS land applied at agronomic rates in Washington. Biosolids are applied to less than 1 percent of state farmland on an annual basis. Applications occur only on permitted fields with rates based on crop type, yield, biosolids nutrient content, and site specific soil analysis. PFAS in Washington biosolids result exclusively from domestic sources and concentrations are likely to be very low. Mean application rates result in soil dilution exceeding 1000-fold in the top two feet. State regulations regarding site restrictions also limit the pathways of exposure. These conditions combined with available data indicate health risks directly attributable to biosolids-sourced PFAS from land application in Washington are low.



## Biosolids Policy Discussion

Biosolids management entities include private business, public utilities, and regulatory agencies. Issues regarding contaminants of "emerging concern" have occurred numerous times. The focus of concern has included a variety of categories such as pesticides, dioxins, PBDE's, antimicrobial compounds, and pharmaceuticals. Typically, the concentrations of these chemicals in biosolids have been exceedingly small and until recent years analytical techniques did not afford consistent identification and quantification. Current analytical reports on PFAS indicate identifiable concentrations in parts per billion and parts per trillion in a variety of media, drinking water in particular. This has renewed concern over the presence of contaminants in biosolids.

Per- and Polyfluorinated Alkyl Substances are nearly ubiquitous in modern society and Washington biosolids will likely show trace concentrations of PFAS. However, trends in the literature regarding PFOS/PFOA concentrations have shown significant decreases in biosolids—primarily attributed to reduced production. If trace concentrations of PFAS are found in Washington biosolids it will largely reflect the domestic exposure people receive in their homes and from the products they use. As such, upstream source reduction--reduced use of products containing these compounds—will be the direct means of lowering PFAS exposure for Washingtonians.

Use of hypothetical leaching models with unrealistic input parameters may calculate unachievable soil contaminant concentration limits. Several states are currently considering a variety of PFAS threshold values for soil based on such modeling. Some of these values for PFAS concentrations in soil may exceed local background levels making them unrealistic and ultimately impossible to implement as a regulatory standard. Setting unrealistic (and thus unenforceable) contaminant thresholds undermines public support for regulation. Ecology should be cautious of implementing extremely low *calculated* contaminant thresholds such as the soil levels being considered in Alaska without field verification data.

Very low regulatory limits for PFAS soil concentrations that are widely applicable could have direct and significant adverse impacts to businesses and municipalities managing biosolids and other residuals. The *perception of risk* resulting from extremely low concentrations that may not have scientifically demonstrated human health risks could also have adverse impacts on generators. The economic and management impacts would extend to a variety of end users of biosolids and compost products. This may result in hesitancy by generators to publically release their proprietary analytical results that are not required by rule.

Risk assessment of biosolids land application requires appropriate analytical methods, modeling of biosolids-related contaminant transfer to soil and groundwater, and toxicological data related to clearly identified pathways of exposure for Washington residents.

## Recommendations

Contaminant assessment by its nature is dependent upon reliable data. Collaborating with our state universities and stakeholders is important for establishing protocols, acquiring defensible data, vetting the range of issues and considerations related to PFAS, and assessing risk related to biosolids land application in Washington. The following are keys to success:

- Establish biosolids and soil sample collection and handling methods;
- Use of the EPA validated analysis method for biosolids;
- Selection of laboratories & accreditation for the method and matrix;
- Credentialed third-party review of the raw data from analysis;
- Compilation of the analysis data along with statistical review.
- Land application sites investigated for PFAS need to mimic rates and practices under current rules;
- Evaluate realistic exposure pathways;
- Risk modeling using realistic input values.

- Broad or statewide assessments of risk related to Washington biosolids land application will require data from a variety of generators across a spectrum of WWTP's. Biosolids generators will likely differ in their requirements for sampling and handling of proprietary data. The protocols developed must withstand scientific scrutiny and satisfy the stakeholders. Ecology should collaborate with stakeholders to develop accurate and precise, but initially anonymous results.
- Evaluation of analysis procedures for determining PFAS concentrations in biosolids and soil is yet to be completed by EPA. Biosolids are a dense organic matrix requiring specific laboratory analysis procedures to achieve accurate and precise results. Use of Method 537 drinking water analysis procedures are inappropriate for evaluating biosolids or soils for PFAS. Biosolids analysis for PFAS concentrations must be based on analytical methods validated by EPA.
- Ecology operates a lab accreditation program at Manchester Environmental Laboratory in Port Orchard. This program provides accreditation for labs across the state. Washington's biosolids program currently requires that pollutant and nutrient analysis be conducted using EPA approved methods for biosolids at labs accredited by the Manchester Environmental Laboratory Accreditation program. This same standard should apply for PFAS analysis in biosolids.
- Analysis methods involving tandem mass spectrometry (MS/MS) involve multiple steps and raw data requires interpretation. Quality Assurance and Quality Control review by third-party, credentialed experts will be necessary to validate initial analysis results from laboratories using newly accredited methods. Geographic and temporal variation in data should also be considered and reviewed.
- Biosolids data from a spectrum of generators is essential to assess broad-based risk from biosolids land application. Triple splits of samples should be encouraged in order to assess analytical precision and comparison of different biosolids samples. Geographic and temporal variation should be evaluated.
- Investigations of PFAS soil concentration directly related to Washington biosolids land application requires sampling application sites where rates and procedures mimic current regulatory practices. Sites across the country suspected of high PFAS concentrations have often been associated with extremely high rates, industrial contamination, or have incorporated spiked concentrations of PFAS compounds; often a combination of these factors. Such conditions are not representative of risk from biosolids land application in Washington under current rules.
- Risk evaluation of Washington's biosolids regulations must evaluate realistic exposure pathways. As an example, PFAS transfer to grain in wheat, not just trace amounts in fine roots of the wheat plant, must exist for there to be substantive health risks to consumers of flour from biosolids fertilized wheat.
- Concurrent with Ecology's responsibility of protecting human health and the environment is the need to ensure that regulatory standards are founded on defensible data and science-based risk assessments. Scientific modeling of PFAS transfer from biosolids to soil or groundwater

used by Ecology for risk assessment must include realistic model parameter values and some level of field verification. Washington biosolids regulation in the near term should ensure sound agronomic land application practices on permitted sites where human exposure is limited. It is premature to add or change regulatory limits given the absence of concentration data from Washington biosolids and problems identified with models and their input parameters.

## Implementation Steps for Biosolids Risk Assessment Related to PFAS

1) Plan and allocate staff time related to PFAS and biosolids;
2) The Department of Ecology shall collaborate with NW Biosolids, research institutions, and other stakeholders to establish the protocols and procedures;
3) Ecology will allocate funds for biosolids sample collection and analysis;
4) Ecology will work collaboratively with a variety of generators to analyze biosolids for PFAS using accredited methods and laboratories. There should be an emphasis on triplicate sample analysis in order to evaluate the precision of analysis results;
5) Collect preliminary soil samples from biosolids application sites with known histories that mimic current Washington rules. There should be an emphasis on triplicate samples in order to evaluate the precision of analysis results;
6) Evaluate the basis of contaminant limits set in other states and Canada and provide a report to Ecology management. Such an evaluation should include a review of baseline biosolids data, contaminant models and their parameters, pathways of exposure, and level of uncertainty.

## Performance Measures

1) Establish a schedule to accomplish the implementation steps above;
2) Report out to stakeholders and management at milestone dates established in the schedule;
3) Finalize the sample collection and analysis protocols and procedures;
4) Acquire a baseline PFAS dataset from Washington biosolids using an EPA accepted analysis method. This should occur within one year after Ecology's Manchester Lab accredits two laboratories in Washington for the EPA validated biosolids analysis method;
5) Acquisition of soil data from application site(s) with known histories that mimic current Washington rules. Analysis must be conducted with an EPA validated method for soil;
6) Provide a written review of other state and Canadian PFAS modeling/risk assessment methodologies by 2022.

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